Effects of surfactants Sb and Bi on the incorporation of zinc and carbon in III/V materials grown by organometallic vapor-phase epitaxy

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The incorporation of both dopants and background impurities during the organometallic vapor phase epitaxial (OMVPE) growth of GaAs, GaInP, and GaP has been significantly altered by the use of the surfactants Sb and Bi. Sb and Bi are isoelectronic with the group V host elements, and so produce no independent doping. This paper demonstrates that the incorporation of Zn can be increased by an order of magnitude in GaP to a value of approximately 10^{20} cm^{-3}, the highest value reported to date. Additionally, these same surfactants lead to significant decreases in carbon contamination during growth. At high growth temperatures the reduction can be as large as 100× in GaP. The surfactants also result in marked decreases in autodoping due to S and Si from the substrate. A marker that may help identify the mechanism for these effects is H incorporation. Both Sb and Bi surfactants give rise to increased concentrations of H in the GaP layers. Similar effects are observed in GaInP. However, in GaAs, no H is detected in the layers. One possible explanation for these phenomena is that Sb or Bi increases the surface H concentration. The increased H would have two possible effects on the incorporation of dopants and impurities. (1) Passivation of the Zn acceptor by formation of a neutral Zn-H complex would lead to *increased* incorporation for thermodynamic reasons. (2) Allowing increased desorption of C, S, and Si from the surface by increased formation of volatile hydrides leads to *decreased* incorporation levels. These results suggest a simple and effective method of controlling the incorporation of dopant and impurity atoms by adding a minute amount of surfactant during OMVPE growth. © *2006 American Institute of Physics*.
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I. INTRODUCTION

Incorporation of dopants in III/V semiconductors has frequently presented problems, especially for high band-gap materials such as AlGaInP and AlGaInN. In AlGaInP, Mg and/or Zn acceptors are often unable to produce the high conductivity materials needed for light-emitting diodes, lasers, solar cells, and other devices.[1] The problem is even more serious in the AlGaInN alloys, where the inability to obtain sufficient *p*-type doping levels retarded device development for decades.[2,3] Three factors contribute to these problems: (1) acceptor solubility limits are small, especially in the high band-gap materials,[4] (2) the acceptors may be compensated by H, especially for the high band-gap materials grown by organometallic vapor-phase epitaxy (OMVPE),[2,4] and (3) the acceptor-hole binding energies may be large, causing the hole concentration to be much less than the acceptor concentration.[3] These problems motivate modification of the OMVPE growth process to allow increased acceptor incorporation.

Additionally, unintentional impurities, particularly oxygen and carbon, have presented an obstacle for the OMVPE growth of III/V materials for decades.[5] Carbon, from the pyrolysis of the organometallic precursors, is often present at high concentration[6,7] and oxygen has proven to increase nonradiative recombination and is difficult to eliminate, especially in Al-containing materials.[1,8] More recently, carbon in GaN and AlGaN (Ref. 9) has proven to give rise to deep levels leading to highly resistive layers grown by OMVPE. For GaInPN alloys, the high carbon doping levels contained in materials grown by OMVPE have hindered the development of high-performance tandem solar cells.[10–12] The longest minority-carrier lifetimes are obtained only using growth conditions that minimize unintentional carbon and hydrogen contamination.[13] Thus a second major problem facing the OMVPE growth community is the development of simple and practical techniques for the reduction of contamination from undesirable impurities.

An appealing approach to both of these problems is the use of surfactants isoelectronic with either the group III or group V host atoms, which do not themselves act as dopants during OMVPE growth. In previous work, we have shown that the surfactants Sb and Bi, both group V elements that are rejected from incorporation into the solid due to their large size, can be used to change the physical and chemical processes occurring at the growing surface. These surfactants have been used to change the microstructure and the band gap of GaInP.[14] More importantly, for the topics introduced above, Sb and Bi have been found to lead to increased Zn incorporation into GaAs.[15] The mechanism for this increase in Zn incorporation is not well established. More work is required to determine how widespread this phenomenon is and to shed new light on the mechanism.

In the work presented here, the increased Zn incorpora-

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tion in GaAs is confirmed. Even larger increases in Zn doping are observed for GaP. For growth at 650 °C, the Zn doping is found to be increased by an order of magnitude by the use of surfactant Sb, to a value of approximately 10^{20} cm^{-3}, the highest Zn doping reported in GaP. A significant observation that may lead to a better understanding of the mechanism for this effect is the increase of H incorporation that is found to correspond to the increased Zn incorporation. An even more dramatic effect of the surfactants Sb and Bi is the marked reduction in carbon contamination. For GaP grown at 775 °C, a clear decrease in carbon by more than two orders of magnitude is observed. In this case, the decrease in C incorporation corresponds to a sharp drop in the concentration of atomic H incorporated into the GaP layer.

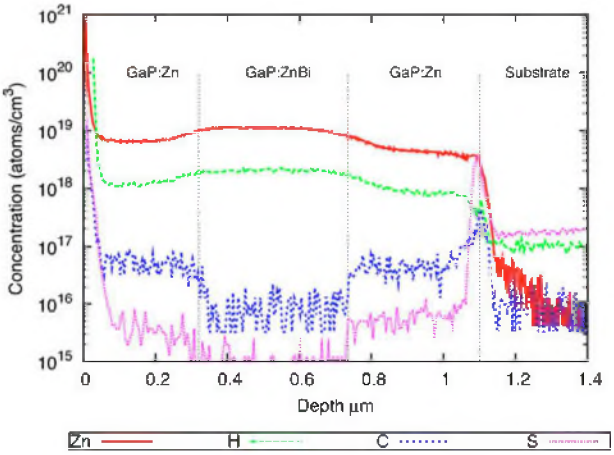

FIG. 1. (Color online) SIMS profile of GaP grown at 650 °C with Bi added only during growth of the middle layer of the three-layer structure.

II. EXPERIMENTAL

Epitaxial GaP layers with surfactants Sb and Bi have been grown by OMVPE in a horizontal, infrared-heated, atmospheric pressure reactor[16] on singular (001) semi-insulating GaP substrates. Trimethylgallium (TMGa), tertiarybutylphosphine (TBP), dimethylzinc (DMZn), trimethylbismuth (TMBi), and trimethylantimony (TMSb) were used as the organometallic precursors. The carrier gas was Pd-diffused hydrogen. The growth temperatures were 650 and 775 °C for GaP with V/III ratios of 60 and 24, respectively. Throughout the experiments a constant growth rate of 1 μm/h was maintained. The zinc/III ratio was varied to compensate for the difference in the Zn distribution coefficient at the two temperatures. At 650 °C the Zn/III ratio was 0.15, while at 775 °C it was increased to 6.9.

GaAs:Zn samples were grown on GaAs semi-insulating substrates using arsine (AsH_3) with Bi as a surfactant. Two growth temperatures of 560 and 680 °C were used.

Single layer GaP samples were grown for Hall effect measurements to determine electrically active carrier concentrations. These samples were 0.75 μm thick, which was verified using growth rates calibrated from secondary ion mass spectroscopy (SIMS) and profilometry results. Samples were grown with either Zn alone or Zn and surfactant. The electrical measurements were performed using the van der Pauw method at room temperature using a 1100 G electromagnet. Ohmic contacts were made to the samples using an In-Zn alloy annealed under N_2 at 350 °C.

SIMS depth profiles were measured on GaP three-layer structures where the surfactant was present only during growth of the middle layer. Growth was stopped between layers for 30 s to adjust flows for the introduction and removal of the surfactant and to allow the flows to stabilize. In addition, SIMS was measured on single-layer GaAs samples to determine the concentrations of Zn and H. Applied Microanalysis Laboratory performed the SIMS measurements using a Cameca IMS4f magnetic sector SIMS instrument. A Cs+ ion beam was used for bombarding the samples. Data was collected using positive and negative detection conditions. The results were calibrated using GaP standards implanted with known doses of the elements of interest. The depth scale was calibrated based on the depth of the SIMS craters.

III. RESULTS

The addition of surfactant Sb (TMSb) or Bi (TMBi) was confirmed to cause an increased incorporation of Zn into GaAs layers grown by OMVPE (Ref. 15) at growth temperatures of both 560 and 680 °C. In contrast with the GaP and GaInP results, discussed below, no H was observed by SIMS analysis of these layers.

We also studied GaInP layers grown at 620 °C and confirmed earlier results[17] showing an increase in Zn incorporation. In the case of GaInP, the incorporation of atomic hydrogen was found to follow the trend of Zn incorporation, i.e., H was observed to increase in the layers grown with either Sb or Bi surfactant. The ratio of H/Zn remained constant with a value of approximately 1:10.

In an effort to observe the effect of increased bonding energy and band gap on the surfactant modulation of doping phenomena, similar experiments were carried out in GaP. Two temperatures, 650 and 775 °C, one near the bottom and one near the top of the range of normal growth conditions, were used in an effort to elucidate the processes involved.

Figure 1 shows the SIMS profile of a GaP three-layer structure, grown at 650 °C using a Zn/III ratio in the input vapor of 0.15, consisting of sequential 0.25 μm layers all grown with the same vapor concentration of DMZn, but with Bi added only during growth of the middle layer. As for GaAs and GaInP, the presence of Bi on the surface during OMVPE growth of GaP leads to an increase in Zn incorporation by a factor of approximately 3. In this figure, the H concentration is seen to follow the Zn incorporation, i.e., H incorporation also increases by approximately 3× in the layer grown with Bi. Strikingly, the ratio of H to Zn remains virtually constant with a value of approximately 1:5 in the GaP layers grown both with and without surfactant. In the graded transition regions, Zn has apparently diffused from the middle layer (grown with Bi) to the surrounding layers

TABLE I. Comparison of free hole concentration from room-temperature Hall effect measurements and the concentrations of the acceptors Zn and C measured using SIMS. All concentrations have units of cm^{-3}. C and Zn concentrations are from SIMS measurements and the hole concentrations are from Hall Effect measurements.

Growth temperature	Surfactant	Zn concentration	C concentration	Hole concentration
650	None	5×10^{18}	4×10^{16}	2×10^{19}
650	Sb	8×10^{19}	3×10^{16}	1×10^{19}
650	Bi	1.1×10^{19}	$\sim8\times10^{16}$	2×10^{19}
650	None	None	4×10^{16}	Small $\ll\times10^{18}$[a]
775	None	8×10^{16}	$0.4-2\times10^{17}$	4×10^{18}
775	None	1×10^{19}	1.7×10^{18}	3×10^{19}
775	Sb	5×10^{17}	3×10^{16}	2×10^{18}
775	Sb	1.2×10^{19}	2×10^{16}	3×10^{19}
775	Bi	—	—	4×10^{18}
775	Bi	9×10^{18}	6×10^{17}	3×10^{19}

[a]Ohmic contacts could not be formed.

(grown without Bi). A similar amount of Zn diffusion is observed into the substrate. The H to Zn ratio remains nearly constant even in the diffused region.

The SIMS profile of Fig. 1 also shows an abrupt decrease in the carbon contamination level in the GaP layer grown with Bi. The carbon doping level in the GaP layer grown at 650 °C is seen to be approximately 4×10^{16} cm^{-3}. The surfactant Bi leads to a decrease in the carbon concentration to $<10^{16}$ cm^{-3}. The concentration of sulfur in the layer, from autodoping of impurities outgassed from the sides and backside of the substrate, is also decreased by the presence of Bi.

For a single layer of GaP grown at 650 °C with the same Zn concentration in the vapor without surfactant, Hall effect measurements indicate a hole concentration of 2×10^{19} cm^{-3}, similar to the Zn concentration of approximately 5×10^{18} cm^{-3} measured in the SIMS profile. The free hole concentrations are compared with the SIMS results from the samples studied in Table I. The hole concentrations are consistently 2–4 times greater than the Zn concentration measured by SIMS. This systematic variance must be due to errors in either the Hall effect or SIMS measurements, since it is otherwise impossible to explain a hole concentration exceeding the acceptor concentration at these doping levels.

Figure 2 shows that the effect of Sb on Zn incorporation in GaP grown at 650 °C is even more dramatic than for Bi. The Zn doping level in the layers grown without Sb is similar to the results shown in Fig. 1, approximately 5×10^{18} cm^{-3}. However, with Sb present during growth, the Zn incorporation is increased by more than an order of magnitude to a value of 8×10^{19} cm^{-3}. This is the highest Zn doping level reported for GaP.[18,19] Again, as was the case in layers grown with Bi, the surfactant Sb causes a nearly parallel increase in the H incorporation into the solid. However, the H:Zn ratio in the layer grown with Sb present is approximately 1:45, much smaller than for Bi. Similar to the results for layers grown with Bi, the addition of Sb during growth results in a significant decrease in the concentrations of both C and S.

For a thick layer grown at 650 °C with Sb added, the hole concentration was measured to be 1×10^{19} cm^{-3}, as seen in Table I, which is much smaller than the value of 8×10^{19} cm^{-3} for the Zn concentration from the SIMS profile. Apparently, not all of the Zn incorporated is electrically active. Electrochemical *C-V* profilometry data show a clear increase in the hole concentration by a factor of 10 in the middle layer of the three-layer structure shown in Fig. 2. But again, the measured *p* concentrations are much lower than the Zn concentrations measured by SIMS.

To probe the mechanisms leading to the phenomena observed for GaP grown at 650 °C, similar experiments were performed at a higher growth temperature of 775 °C. The concentration of DMZn in the vapor was increased significantly to compensate for the increased rate of Zn desorption from the surface during growth.[20] A value of Zn/III of 6.05 was used for the samples, producing the SIMS data shown in Figs. 3 and 4.

Figure 3 shows the effects of Bi on the Zn incorporation in a three-layer GaP structure grown at 775 °C. In the layers grown without Bi, we observe a high C contamination level of 1.7×10^{18} cm^{-3}. Again, as for the GaP grown at lower temperatures, the presence of Bi, during growth of the middle layer, results in a significant decrease in the C level by more than a factor of 2. Surprisingly, however, the effect

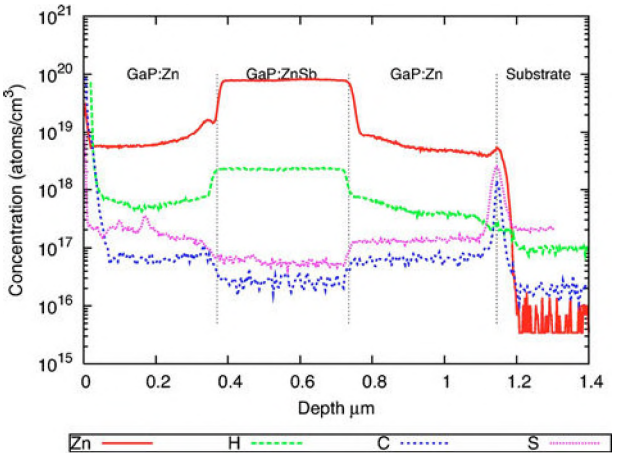

FIG. 2. (Color online) SIMS profile of GaP at 650 °C with Sb added only during growth of the middle layer of the three-layer structure.

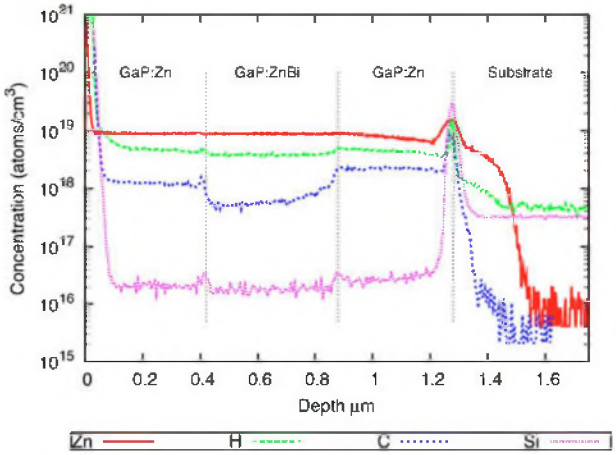

FIG. 3. (Color online) SIMS profile for GaP grown at 775 °C with Bi added only during growth of the middle layer of a three-layer structure.

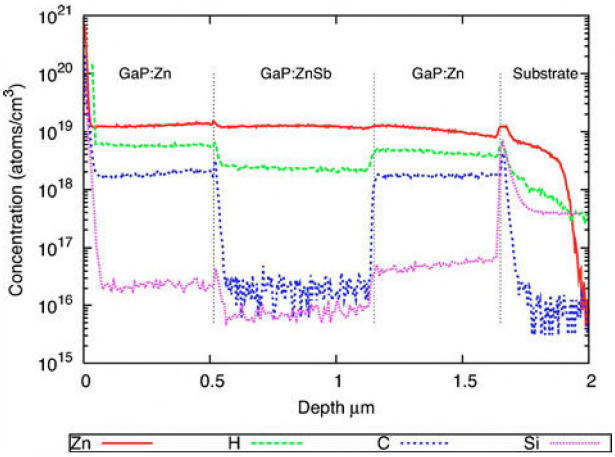

FIG. 4. (Color online) SIMS profile for GaP at 775 °C with Sb added only during growth of the middle layer of a three-layer structure.

of Bi on Zn concentration appears to be insignificant at 775 °C. In the layers grown both with and without Bi, the H:Zn ratio is observed to be approximately 1:2, considerably higher than the values in the GaP layers grown at 650 °C. The SIMS results clearly show that the H concentration in the solid is more than twice as high in the layers grown at 775 °C than for those grown at 650 °C due to the increased amount of C contamination, as discussed below. A slight reduction in the Si autodoping level from the substrate is also observed. No S incorporation into the GaP epitaxial layers is observed for growth at these higher temperatures. Si doping is known to increase while S doping decreases as the growth temperature is increased.[20]

The effect of Sb during growth at 775 °C is shown in Fig. 4. As with Bi, the surfactant Sb appears to have very little effect on the Zn incorporation. However, the C concentration is observed to drop from approximately 2×10^{18} cm^{-3} in the layers grown without surfactant to a value of $< 2\times10^{16}$ cm^{-3}, most likely the SIMS detection limit, in the layer grown with Sb present. The H incorporation also decreases when Sb is added to the system during growth. This can be explained by the combination of Zn and C doping. Clearly, H incorporation is larger in the layers highly doped with C, which accounts for the drop in H in the layer grown with Sb added. The layer containing the small C concentration has a H:Zn ratio of approximately 1:5, a value similar to those reported above for layers grown at 650 °C. The values of the H:Zn ratio as observed in these experiments are summarized in Table II. The increased H in the layers grown without Sb indicates a H:C ratio of approximately unity, much larger than the H:Zn ratios. The data in Fig. 4 also show a clear decrease in Si doping for the layer grown with Sb.

A significant observation from both Figs. 3 and 4 is that Zn diffuses approximately 0.3 μm into the substrate during growth at 775 °C. This offers a possible explanation of the apparent lack of an effect of Sb and Bi on Zn incorporation at 775 °C observed in Figs. 3 and 4. At this temperature, Zn diffuses out of the 0.25 μm thick middle layer and into the adjoining layers on either side, thus giving the appearance

TABLE II. Comparison of Zn:H and Mg:H ratios in GaAs, GaInP, GaP, and GaN showing the general decrease in acceptor:H ratio with increasing host bond strength

Host material	Acceptor	Surfactant	Growth temperature (°C)	Ratio Zn:H	Reference
GaAs		None, Sb, or Bi	560 and 680	(no H detected)	
GaInP		Sb	620	100	17
GaInP		Bi	620	10	17
GaInP	Zn=1.5×10^{18}	None	620	>100	17
GaP	Zn=7×10^{18}	None	650	5:1 (Bi) 13:1 (Sb)	
GaP	Zn=1.2×10^{19}	Bi	650	5:1	
GaP	Zn=9×10^{19}	Sb	650	33:1	
GaP	Zn=1.3×10^{19}	None	775	2:1 (Bi) 2.2:1 (Sb)	
GaP(substrate) Diffused layer		None	775	4-5:1	
GaP	Zn=1.3×10^{19}	Bi	775	2.2:1	
GaP	Zn=1.5×10^{19}	Sb	775	5.5:1	
GaP	Zn=5×10^{17}	Sb	775	2:1	
GaN	Mg=8×10^{19}	None	500–1150	Mg:H=1:1	21

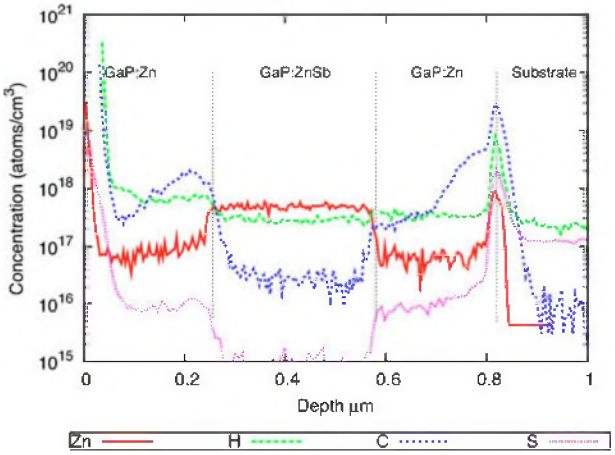

FIG. 5. (Color online) SIMS profile of GaP grown at 775 °C with a reduced Zn/III of 0.069. Sb is added only during growth of the middle layer of a three-layer structure.

that no change in the Zn doping is produced by adding Sb (or Bi). Another significant feature of the Zn diffusion into the substrate is that H accompanies the Zn with a H:Zn ratio of approximately 1:4–5 in both cases, the same approximate H:Zn ratio observed in the layer grown using Sb at 775 °C. This phenomenon appears to demonstrate that H tracks Zn incorporation with an approximate constant ratio of H:Zn, which might indicate the equilibrium Zn-H concentration under these specific conditions. Unexplained is the difference between the H:Zn ratio of the layers grown with Sb and Bi at 775 °C. Interestingly, the increase in temperature from 650 to 775 °C does not markedly change this ratio.

To better understand the Zn, C, and H incorporation at 775 °C, a three-layer structure was grown with a decreased Zn/III ratio of 0.069 in the vapor. As shown in Fig. 5, this decreased DMZn partial pressure results in a Zn concentration in the layers grown without Sb of approximately 8×10^{16} cm^{-3}, more than two orders of magnitude lower than for the data shown in Fig. 4. Importantly, the increase in Zn doping by a factor of 5× produced by the addition of surfactant Sb to the system is again clearly observed. This clearly indicates that the disappearance of the effect of Sb on Zn doping seen in Figs. 3 and 4 occurs only at very high Zn doping levels. As discussed above, this may be due to Zn diffusion. As the Zn concentration decreases, the Zn diffusion length is reduced, as clearly observed at the substrate/epitaxial layer interface. This significant decrease in Zn diffusion occurs because the diffusion coefficient is strongly dependent on Zn concentration due to the interstitial diffusion mechanism.[22] This suggests that Zn diffusion between the layers in Figs. 3 and 4 is larger than between the first layer and the substrate, due to the increased Zn incorporation induced by the Sb and Bi.

From the SIMS data in Fig. 5 it appears that the H:C ratio in the layers grown without surfactant is less than or equal to 1 and the H:Zn ratio in the layer grown with Sb present is approximately 1:2. Similarly to the data in Fig. 4, the Si concentration is decreased by the addition of surfactant Sb.

For a single layer grown using the same conditions as the middle layer of the sample shown in Fig. 5, Hall effect measurements give a hole concentration of 2×10^{18} cm^{-3}, as shown in Table I, similar to the value of 5×10^{17} cm^{-3} for the Zn concentration from SIMS measurements.

IV. DISCUSSION

A number of important observations concerning the effects of the surfactants Sb and Bi on Zn, C, S, and Si incorporation into GaAs and GaP have been made from the experimental data presented: (1) Both Bi and Sb increase the concentration of Zn in GaAs and GaP. The increase is as large as a factor of 10 for GaP grown at 650 °C, giving the highest Zn incorporation levels measured in that material. (2) At low temperatures where the carbon concentration is low, the addition of Sb and Bi increases the concentration of atomic H incorporated into GaP. (3) Under these conditions, the H concentration tracks the Zn concentration in GaP, with ratios of H:Zn that vary with growth conditions, as summarized in Table II, with typical values between 1:2 to 1:5, with the notable exception of the very highly Zn-doped sample grown with the addition of Sb at 650 °C (Fig. 2), where the ratio reaches a value of 1:45. (4) The surfactants Sb and Bi act to decrease the concentrations of C, S, and Si incorporated into GaP. (5) For the GaP samples grown at 775 °C without surfactant, the carbon contamination level reaches values of approximately 2×10^{18} cm^{-3}, which are reduced by a factor exceeding 100 when Sb is added to the system. A smaller reduction in C is produced by the addition of Bi. (6) The C:H ratio of the GaP samples grown at 775 °C is large, approximately 1:1, after accounting for the H incorporation due to Zn. (7) The Zn is typically electrically active, i.e., Hall effect measurements of the free hole concentration are approximately equal to the Zn concentrations determined by SIMS analysis, as summarized in Table I. The exception is the very highly doped sample grown at 650 °C (Fig. 2) where Sb is added during growth. In this case the hole concentration is significantly smaller than the Zn concentration of 8×10^{19} cm^{-3} measured by SIMS and *C-V* profiles. (8) The C appears not to be electrically active, i.e., the GaP layers grown without Zn at 775 °C are not high conductivity *p* type, since ohmic contacts could not be formed to these samples. (9) The H:Zn ratio is clearly larger in GaP than in GaInP (Ref. 17) and the ratio in GaAs is approximately zero, i.e., no H was detected in the SIMS profiles.

A. Zn incorporation

The first step in analyzing the effects of surfactants on Zn incorporation, summarized above, is to attempt to determine whether the increased H incorporation induced by the surfactant (Sb or Bi) is due to the surfactant *per se* or is due to the increased Zn concentration incorporated into the solid, i.e., is the observed increase in H incorporation a cause or an effect of the higher Zn incorporation. First, it should be realized that the surface H comes from a balance of H produced during pyrolysis of TBP and H desorption as H_2. Intuitively, one expects less H on an Sb or Bi covered surface simply because the Sb–H and Bi–H bonds are much weaker than the P–H bonds on the typical reconstructed GaP surface

formed during OMVPE growth, which would result in increased H_2 formation and desorption. However, the strength of the dimer bonds must also be considered in this analysis. First principles calculations to determine the minimum energy configurations for the clean and surfactant-covered surfaces are relatively straight-forward. However, the definitive answer must also include temperature (entropy). Such calculations are currently underway in our group.

The phenomena involved have been broken down into thermodynamic effects followed by a discussion of kinetic effects. First, considering thermodynamic effects, the Zn incorporation might be postulated to increase H incorporation simply due to the well-known acceptor-H attraction. H is known to form a complex with the group II acceptors, with the H bound to a group V nearest neighbor of the acceptor, resulting in compensation of the acceptor. Such acceptor compensation has been reported in several III/V semiconductors.[23,24] Thus any surfactant effect leading to increased Zn incorporation would result in increased H incorporation. If this is the only cause of H incorporation, the H concentration provides no clues about the mechanism responsible for the increased Zn incorporation due to surfactant Sb or Bi. This hypothesis would explain the nearly constant H:Zn ratio, even when Zn has diffused from the epitaxial layer into the substrate. To test this hypothesis, we attempted to measure the temperature dependence of the H:Zn ratio in the solid. At higher temperatures, the Zn:H complex would dissociate; thus less H would be observed in the solid. The experiments designed to reveal this critical effect were impossible to interpret due to the increased concentration of C incorporated in GaP at higher growth temperatures, which results in a second, independent mechanism leading to increased H incorporation at higher growth temperatures. Thus this experiment sheds little light on the mechanism by which Sb or Bi increases Zn incorporation.

On the other hand, the change in surface bonding induced by the surfactant may lead to an increase in atomic H adsorbed at the surface or, perhaps, just at the step edges. This increase in available surface H at the position of Zn incorporation would facilitate Zn incorporation at high levels based on thermodynamic arguments. High *p*-doping levels require movement of the Fermi level near to or into the valence band when the dopants are incorporated as charged species.[25] This leads to an increase of the free energy of the system. Zunger[26] has suggested that such an increase in the Fermi level would lead to the formation of compensating native defects for GaP and AlGaInP alloys to decrease the total energy of the system. However, incorporation of neutral Zn–H complexes would provide a more likely alternative that would accomplish the same goal. In fact, compensation of Zn acceptors in GaP by atomic H has been clearly demonstrated by Mizuta *et al.*[23]

A closely related thermodynamic mechanism that might explain the effect of Sb or Bi on Zn incorporation is related to Fermi level pinning at the surface. It has been well established that surface pinning of the Fermi level can have an important effect on dopant incorporation.[27] However, we have no information about the effect of Sb or Bi on surface Fermi level pinning in either GaAs, GaInP, or GaP.

If the increased Zn incorporation were entirely due to either mechanism involving a minimization of the chemical potential of holes, we would predict that the increase in H induced by the surfactant would be equal to the increase in Zn. The experimental data, summarized in Table II, clearly show that the change in H concentration is always less than the change in Zn. A possible explanation is that following growth, during cooldown, H is removed from the surface. Then the dissociation of a significant fraction of the Zn–H complexes in the solid would produce H that would diffuse to the surface, where it would be evaporated into the vapor phase as H_2.

Either mechanism would be consistent with the lack of H in the Zn-doped GaAs samples grown at 560 and 680 °C. As discussed above, it is believed that the H in the Zn–H complex bonds to a group V atom bonded to the Zn, which is located on a Ga site.[24] Since the As–H bond is significantly weaker than the P–H bond,[5] the Zn–H complex would dissociate more rapidly and more completely in GaAs and virtually all of the H would be lost from the solid. Either mechanism is also consistent with independent observations related to doping using the similar acceptor Mg in GaN. The H:Mg ratio in GaN, where the V–H bond is even stronger than for GaP, is nearly unity.[21] In this case, special, post-growth annealing in nitrogen is required specifically to activate the Mg by dissociation of the Mg–H complex and out-diffusion of the hydrogen.[2,3] Either mechanism could also account for the nearly constant H:Zn ratio in all of the layers, including in the substrate where Zn has diffused at 775 °C. Either mechanism is also consistent with the hole concentrations measured, i.e., the Zn is typically nearly uncompensated at both temperatures.

Finally, the effect of Sb or Bi on the incorporation energy of Zn on a Ga site just below the surface would be expected to play a key role in the effects of surfactants on Zn incorporation. No experimental data are available to allow the assessment of this factor; thus first principles calculations are currently underway in our group to determine the dependence of the incorporation energy on the surface composition and bonding.

We turn now to possible kinetic mechanisms to explain the effects of surfactants Sb and Bi on Zn incorporation. A possible mechanism is related to the kinetics of Zn incorporation at step edges. Unfortunately, no information is available that would allow us to probe this mechanism further.

A second mechanism is related to the pyrolysis of the Zn precursor, DMZn. This is a factor unlikely to affect the results since DMZn pyrolysis at the growth temperatures used in these experiments is expected to occur rapidly by homolysis, so will not be affected by the surface chemistry.

An important feature of the data that needs to be addressed is the inactivity of Zn in the layers grown at 650 °C using surfactant Sb. From the compensation of the Zn and the very low H:Zn ratios measured, it is concluded that much of the very high Zn concentration in that layer is in a form other than Zn on a Ga site. This could include interstitial Zn, which would be a donor, or a neutral Zn complex not considered here, or perhaps, precipitates.

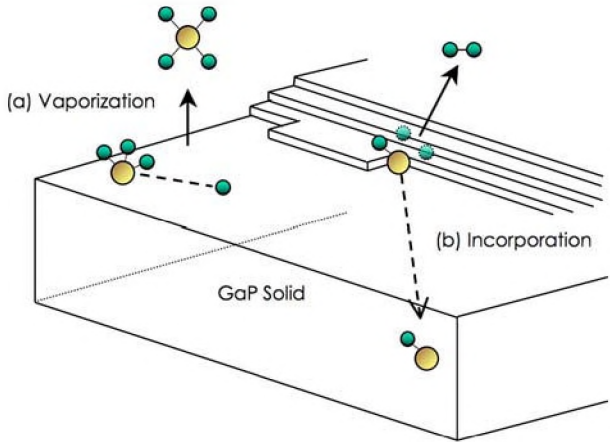

FIG. 6. (Color online) Schematic illustration of two fates for CH_3 adsorbed on the surface: (a) combination with H to form CH_4 in the vapor and (b) loss of H_2 at incorporation site to produce C-H in the solid.

B. Residual impurity incorporation

The behavior of carbon incorporation when Sb or Bi is added to the system might be a natural consequence of the additional levels of atomic H adsorbed at the surface. For OMVPE growth using trimethyl-III precursors, a significant concentration of methyl radicals on the surface during growth is to be expected.[5] The surface CH_3 radicals have two possible fates, as indicated in the schematic diagram shown in Fig. 6. The CH_3 can recombine with a surface H, creating CH_4 which is rapidly desorbed. If the CH_3 radical can attach at a step site and lose one or more H ligands before desorbing, it will result in the incorporation of C into the solid. The SIMS data suggest that the entity incorporated is actually the C–H complex, since the H:C ratio appears to be approximately unity. In addition. Hall effect and capacitance-voltage data indicate that the hole concentrations are only a small fraction of the C incorporated as indicated in Table I. This might be postulated as due to self-compensation, except that previous work clearly shows that C in GaP occupies the P site.[28,29] Thus the compensation of C is most likely due to H. Clearly, only a small fraction of the C–H complexes dissociate, since the free hole concentrations are consistently much lower than the C concentration in samples not doped with Zn. The H is bonded directly to the C in GaP in *p*-type material, resulting in effective neutralization of the carbon.[30] Apparently, the energy necessary to dissociate the C–H complex is significantly larger than for the Zn–H pair.

The behavior of C in GaP appears to be similar to that in GaN, where samples contaminated with C show high resistivity.[12] The effect of growth temperature is readily explained using the model described above. At lower temperatures, the probability that the C–H bond in CH_3 will break before desorption is much smaller than at the higher temperatures.

The higher levels of adsorbed atomic H would also explain the reduction in S and Si produced by adding Sb or Bi to the surface. The increased concentration of surface hydrogen would lead to the formation of volatile SiH_4 and H_2S, both of which are readily desorbed. This mechanism would also explain the reduction in oxygen due to Sb or Bi reported by Chapman *et al.*[17]

An alternate possible explanation of the decrease in C caused by Sb or Bi on the surface is simply methyl radical desorption. The CH_3 is more weakly bound to an Sb or Bi covered surface, since both the Sb-CH_3 and the Bi-CH_3 bonds are considerably weaker than the P-CH_3 bond. The increased rate of methyl radical desorption would explain the reduced carbon incorporation into the solid. Similar explanations would account for the reduction in the Si incorporation, since Si probably bonds to the surface group V atoms. The situation is less clear for S and for O, where bonding to the surface group III atoms would be expected. In any case, the observation that carbon decreases with the use of surfactants Sb and Bi is potentially highly useful to ameliorate the problems associated with carbon impurities discussed in the introduction.

V. SUMMARY

The results presented in this paper demonstrate that the surfactants Sb and Bi, both isoelectronic with host P, can be used to significantly alter the incorporation of both intentional dopants and impurity elements into GaP. The surfactants have the beneficial effect of increasing Zn incorporation. For growth at 650 °C, this results in a Zn incorporation level of nearly 10^{20} cm^{-3}, the highest reported for GaP, although activation of the Zn at these high levels is incomplete. H incorporation is seen to track Zn incorporation, with H:Zn ratios ranging from 1:2 to 1:5. For growth at 775 °C, the addition of surfactant Sb causes a reduction in the carbon concentration by a factor greater than 100. The dopants S and Si, originating from the substrate, are also reduced by addition of surfactant Sb or Bi.

The possibility of an additional concentration of available H on the surface when Sb or Bi is added as a surfactant is a simple explanation for the increased incorporation of Zn and the decreased incorporation of C, S, Si, and O into the solid. However, the lack of a detailed knowledge, either experimental or theoretical, about the effects of Sb and Bi on H coverage on the reconstructed surface or at the step edges, Zn incorporation energy, Fermi level pinning at the surface, and attachment of Zn at step edges leaves us unable to make a definitive determination of the mechanism at this point. It is anticipated that first principles calculations of the energies involved will assist in determining the mechanisms for the observed effects.

The judicious use of surfactants during OMVPE growth can be a powerful factor for the control of the surface processes, leading to dopant incorporation into the solid.

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